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RESEARCH AND DEVELOPMENT OF RARE EARTH-TRANSITION METAL ALLOYS AS PERMANENT-MAGNET MATERIALS

A. E. Ray and K. J. Strnat

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13. ABSTRACT

Mixed intermetallic phases of the type $R_2(Co_{1-x}Fe_x)_{17}$ with R=Ce, Pr, Nd, Sm, Y, and MM (Ce-rich mischmetal) are being studied as potential permanent magnet materials. Except for R=Nd, all show ranges of x in which the crystallographic c-axis is the easy axis of magnetization. During the present period, these ranges have been more precisely defined and quantitative measurements of the saturation magnetization and crystal anisotropy constants initiated. It is concluded that some of these alloys are indeed promising candidate materials for improved rare earth-cobalt magnets.

The composition dependence of selected metallurgical and magnetic properties of phases of the type $Nd_{1-x}R_xCo_5$, where R=Ce, Pr, and Y, are under investigation. Peritectic melting temperatures, lattice constants, Curie temperatures, and saturation-magnetization measurements are reported. Single crystals of several of the mixed phases have been prepared and saturation magnetization and room-temperature anisotropy measurements on these have been initiated. ( )

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Successful attempts were made to enhance the intrinsic coercive force of Sm_2Co_{17} by sintering with a Sm-Co addition. Sintering of compacts made from Sm_2Co_{17} powder of $_MH_c < 1000$ Oe with Sm60/Co40 yielded magnets with coercive forces of up to 9600 Oe.

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RESEARCH AND DEVELOPMENT OF RARE EARTH-TRANSITION
METAL ALLOYS AS PERMANENT-MAGNET MATERIALS

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Details of illustrations in
this document may be better
studied on microfiche

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FOREWORD

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ABSTRACT

Mixed intermetallic phases of the type $R_2(Co_{1-x}Fe_x)_{17}$ with R = Ce, Pr, Nd, Sm, Y, and MM (Ce-rich mischmetal) are being studied as potential permament magnet materials. Except for R = Nd, all show ranges of x in which the crystallographic c-axis is the easy axis of magnetization. During the present period, these ranges have been more precisely defined and quantitative measurements of the saturation magnetization and crystal anisotropy constants initiated. It is concluded that some of these alloys are indeed promising candidate materials for improved rare earth-cobalt magnets.

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New cobalt-rich intermetallic phases have been found in three binary rare earth-cobalt alloy systems. Single phase alloys of Ce_5Co_{19}, Pr_5Co_{19}, and Nd_5Co_{19} have been prepared. Lattice constants for the rhombohedral forms of these phases are reported. The Curie temperatures of these phases were also measured and found to lie between those of the corresponding RCo_5 and R_2Co_7.

Successful attempts were made to enhance the intrinsic coercive force of milled RCo_5 alloys with R = Nd and Di (didymium) by sintering with Pr-Co and Sm-Co additions. Sintering $NdCo_5$ powders with as-ground coercive force of $_MH_c$ = 190 Oe with Pr-Co additive raised the coercive force to $_MH_c$ = 4000 Oe; the coercive force of $DiCo_5$ could be increased from 130 Oe to $_MH_c$ = 10,280 Oe. Sintering of compacts made from Sm_2Co_{17} powder of $_MH_c$ <1000 Oe with Sm60/Co40 yielded magnets with coercive forces of up to 9600 Oe.

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MAGNETIC PROPERTIES OF $R_2(Co, Fe)_{17}$ PHASES

A. INTRODUCTION

Mixed intermetallic phases of the type $R_2(Co_{1-x}Fe_x)_{17}$ are being studied as possible high-energy, high coercive-force permanent magnet materials. For a ferromagnetic substance to qualify for this application, three basic magnetic properties must be favorable: saturation magnetization and Curie temperature must be high, and the magnetocrystalline anisotropy must be such that, ideally, a single direction in the crystal lattice is strongly preferred by the spontaneous magnetization vector. The inter-metallic compounds of the type RCo_5 between rare earth metals (symbol R) and cobalt meet these conditions quite well. The intermetallic phases, R_2Co_{17}, have even higher saturation values and Curie points.[1, 2] However, the first compound in this class on which room temperature anisotropy measurements were made, Y_2Co_{17}, has a much lower anisotropy constant, K_1, than the RCo_5 phases. Moreover, K_1 is negative,[3, 4] so that the c-axis is magnetically hard and the easy directions are in the basal plane. In view of this discouraging early result and because of the exciting promise of the RCo_5 phases, further study of the R_2Co_{17} compounds was delayed for several years. It did become known that Sm_2Co_{17} has the favorable easy-axis anisotropy,[5] but its anisotropy field is only about 25% of that of $SmCo_5$.

In contrast to the RCo_5 phases, which have no "RFe_5" counterparts, there is a family of rare earth-iron compounds of the type R_2Fe_{17}.[6] While

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these have higher absolute saturation moments than their cobalt equivalents, they have lower Curie points.[7] The R_2Co_{17} and R_2Fe_{17} phases of most of the rare earth elements were recently investigated[8] to find if any, other than Sm_2Co_{17}, had the desired magnetic symmetry. It was found that all of the R_2Fe_{17} phases and most of the R_2Co_{17} phases showed easy-basal-plane anisotropy. Only the R_2Co_{17} phases with R = Sm, Er, and Tm were observed to have the c-axis as the easy direction of magnetization.

We were reasonably confident on the basis of theoretical considerations that by preparing ternary phases of the type $R_2(Co, Fe)_{17}$, we could achieve a favorable compromise between the high saturation magnetizations of the R_2Fe_{17} and the high Curie temperatures of the R_2Co_{17} phases. It was also recognized that the key property for permanent magnet applications is a large, uniaxial magnetocrystalline anisotropy and that the mixing of cobalt and iron in the T-sites of R_2T_{17} compounds in alloying combinations of the type $R_2(Co_{1-x}Fe_x)_{17}$ should strongly influence the magnetocrystalline anisotropy. We also thought that this mixing of Fe and Co may induce a favorable magnetic symmetry in these phases even where it does not exist for the terminal phases of the quasi-binary systems, R_2Co_{17} and R_2Fe_{17}.

Initial screening tests were concentrated on the Curie temperatures and magnetic symmetries. The results of these tests[9] must be termed extremely encouraging. Our measurements show that while the Curie points are monotonically lowered by the substitution of iron for cobalt, the absolute Curie temperatures remain very high, above 600°C, for iron substitution

up to 50% or more. Moreover, of the six quasi-binary R_2Co_{17}-R_2Fe_{17} systems with R = Ce, Pr, Nd, Sm, Y, and MM studied, all except R = Nd display wide composition ranges in which the c-axis indeed becomes the easy direction of magnetization.

During this reporting period, we have defined more precisely the compositional ranges in which this easy-c-axis symmetry prevails and have conducted quantitative measurements of the saturation magnetization and crystal anisotropy constants for alloys lying in these ranges.

B.   EASY DIRECTIONS OF MAGNETIZATION IN TERNARY $R_2(Co, Fe)_{17}$ PHASES (Shanley, Harmer, Ray)

The alloys were prepared by arc melting of the elements followed by vacuum annealing below the peritectic or melting temperatures, as previously described.[9] The crystal axis of easy magnetization was determined from x-ray diffraction measurements on powders aligned in a magnetic field. Powders of -200 mesh (<78 μm) were prepared by mortar grinding and sifting. The particles were premagnetized in a field of 26 kOe, mixed with epoxy resin, and placed in a 6 kOe field to orient the particles while the binder hardened. The needle-shaped samples so produced were placed in a Weissenberg camera and rotating-crystal diffraction patterns were obtained. Vanadium-filtered CrK_{α} radiation was employed. The patterns obtained are typical of those of a strongly textured sample. The crystallographic nature of the axis which preferentially aligned with the applied field was determined by qualitative evaluation of this texture.

The crystal-anisotropy studies revealed that the easy-axis symmetry of $Sm_2(Co_{1-x}Fe_x)_{17}$ alloys is retained up to x = 0.5. When more than half of the cobalt is replaced by iron, the easy direction changes from the c-axis to the basal plane. Substitution of even small amounts of Fe for Co in the systems in which the rare earth is either Ce, Pr, or Y brings about easy c-axis behavior, which again prevails until about 50% of the cobalt is replaced. (In the Pr-system it persists to x = 0.6.) Because of its potential interest in the commercial production of inexpensive magnets, cerium-rich mischmetal (MM) was also investigated. Here the easy c-axis range extends from x = 0.1 to x = 0.45. These results are schematically summarized in Figure 1. Of the six quasi-binary systems investigated, only that in which the rare earth is neodymium exhibits easy-basal-plane symmetry over the entire range from x = 0 to 1.0.

C.   MAGNETIC TRANSITION TEMPERATURES OF $R_2(Co, Fe)_{17}$ PHASES
(Hartings, Mildrum, Strnat)

We have previously reported Curie temperatures for the six $R_2(Co_{1-x}Fe_x)_{17}$ systems with R = Y, Ce, Pr, Nd, Sm and MM determined mainly by differential thermal analysis.[9] During heating or cooling through the Curie temperature, a minor thermal event occurs. If one knows where to look for it, as one does in these systems because of the expected systematic composition dependence of any of the properties, one can determine the temperature of magnetic ordering from the first deviation of the cooling curve from a smooth line. T_c can be precisely located only on the cooling
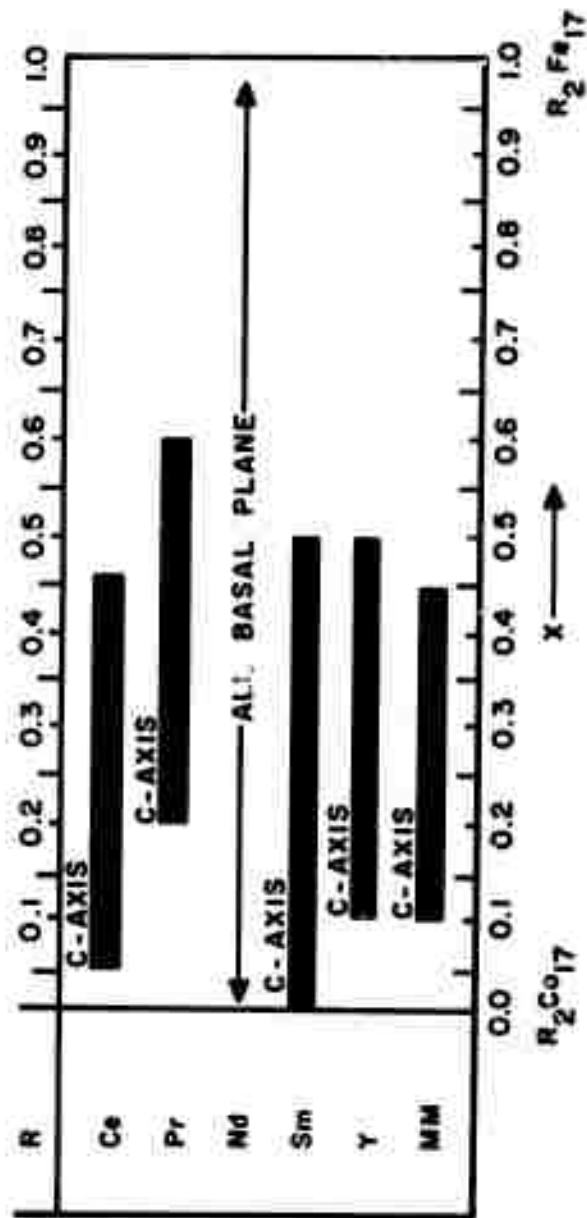
Figure 1. Magnetic symmetry of $R_2(Co_{1-x}Fe_x)_{17}$ phases. Shaded areas indicate the range of x in which the crystallographic c-axis is the direction of easy magnetization.

curve. Due to the second-order nature of most magnetic transitions, DTA heating curves are rather useless in this analysis. The temperature control and measurement system in our DTA apparatus permits the reliable determination of magnetic transition temperatures in this manner only above $400^{\circ}C$. To supplement the DTA results and to extend them to x = 1, where $T_c < 400^{\circ}C$, we had previously performed and included in the last semiannual report several thermomagnetic analyses (TMA) on iron-rich alloys in the Ce-Co-Fe and Sm-Co-Fe alloy systems. The TMA apparatus and the measurement technique were also described in that report.[9] A "TMA spectrum" is a plot of the measured induction voltage (closely related to the initial permeability, μ_i) as a function of temperature.

In the period covered by the present report, TMA of this kind were performed from room temperature upwards on all the alloys available in the $R_2(Co_{1-x}Fe_x)_{17}$ systems where R is samarium or cerium, and from x = 0 to 0.6 in the system with R = yttrium.

The TMA spectra of the Y-Co-Fe alloys are the simplest. Figure 2 illustrates the behavior of $Y_2(Co_{.9}Fe_{.1})_{17}$ which is qualitatively typical for all other alloys in this system. The curve exhibits a pronounced Hopkinson maximum followed by an abrupt drop of the curve on the high-temperature side, and a minor second step at a slightly higher temperature. The shape of the major Hopkinson peak is characteristic of a normal, second-order Curie transition such as that of the simple ferromagnets iron, cobalt or nickel. The curves are very similar on heating and cooling and show no

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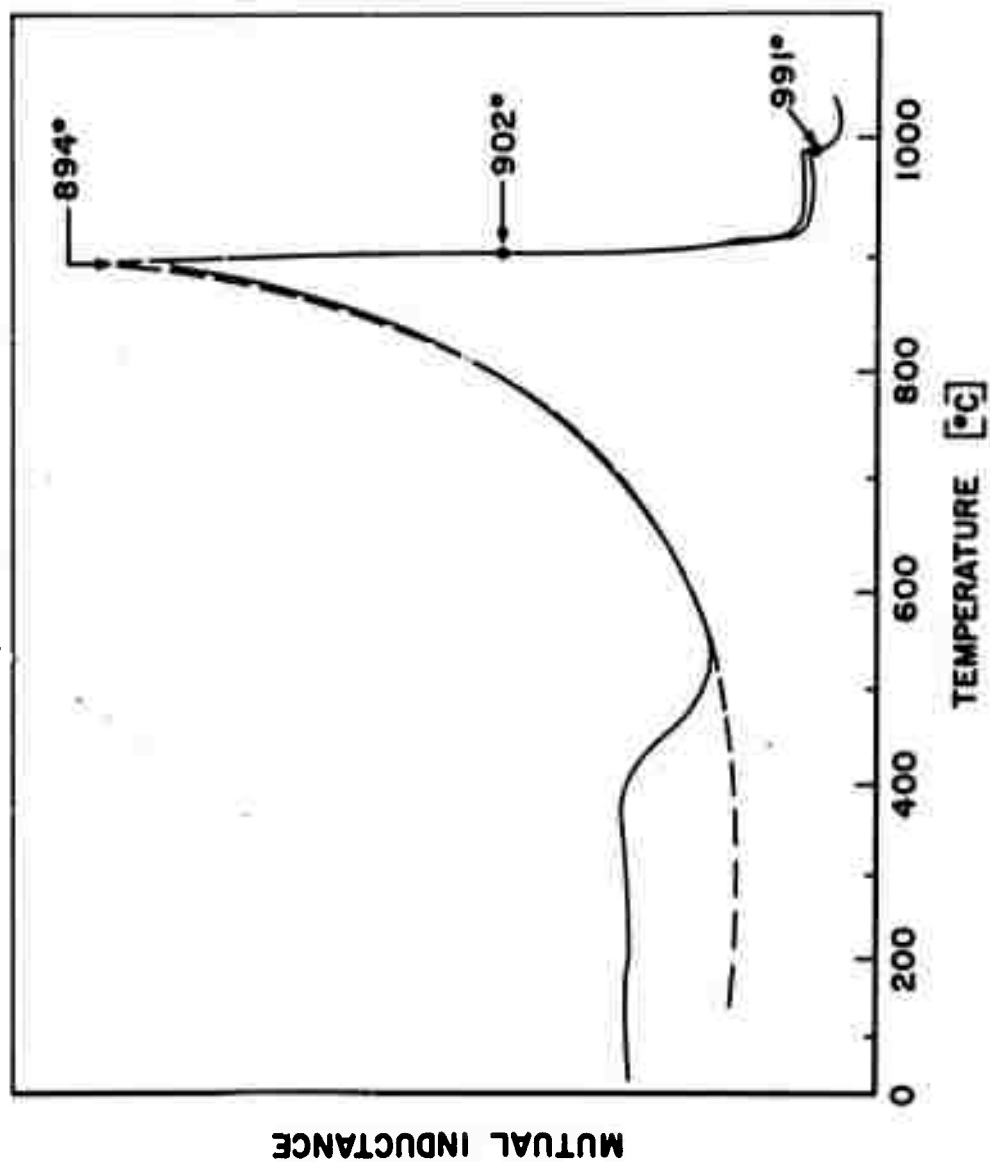
Figure 2. TMA spectrum of $Y_2(Co_{.9}Fe_{.1})_{17}$ alloy. Solid line is the heating curve; dashed line is the cooling curve.

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thermal hysteresis. Repeated cycling consistently gives the same results. In analyzing the curves, we took the point of inflection on the steep slope above the major peak as indicator of the Curie temperature. The results obtained to date are summarized in Figure 3. The T_c data so obtained correspond very closely to those previously determined by DTA.

The position of the minor step has a composition dependence which is quite different from that of the major peak. The step lies above T_c for x = 0 and 0.1, coincides with it for x = 0.2, and then drops rapidly with increasing x to 230°C for x = 0.5. No second step was observed for x = 0.6. By extrapolation one might expect it to occur near -200°C, but we have not yet performed TMA below room temperature. For Y_2Co_{17} (x = 0), the second step coincides with the Curie temperature of pure Cobalt. (The Y_2Co_{17} alloy was not analyzed as part of the present investigation. The data used is from previous work of J. C. Olson.)[10] It had been shown that the "Y_2Co_{17}" alloy on which the TMA was performed contained a small amount of cobalt as a second phase. This suggests that the secondary "TMA event" in the $Y_2(Co, Fe)_{17}$ alloys may also be attributable to a second-phase impurity which is substantially a cobalt-iron alloy. The "event" would then be the Curie temperature of the γ-modification of the Co-Fe binary phase. If this were indeed the case, it would follow that the Fe:Co ratio is greater in this impurity phase than in the main phase. Furthermore, the magnetic results would suggest that the small quantities of yttrium that can be in solid solution in the Co-Fe are capable of stabilizing the face-centered form

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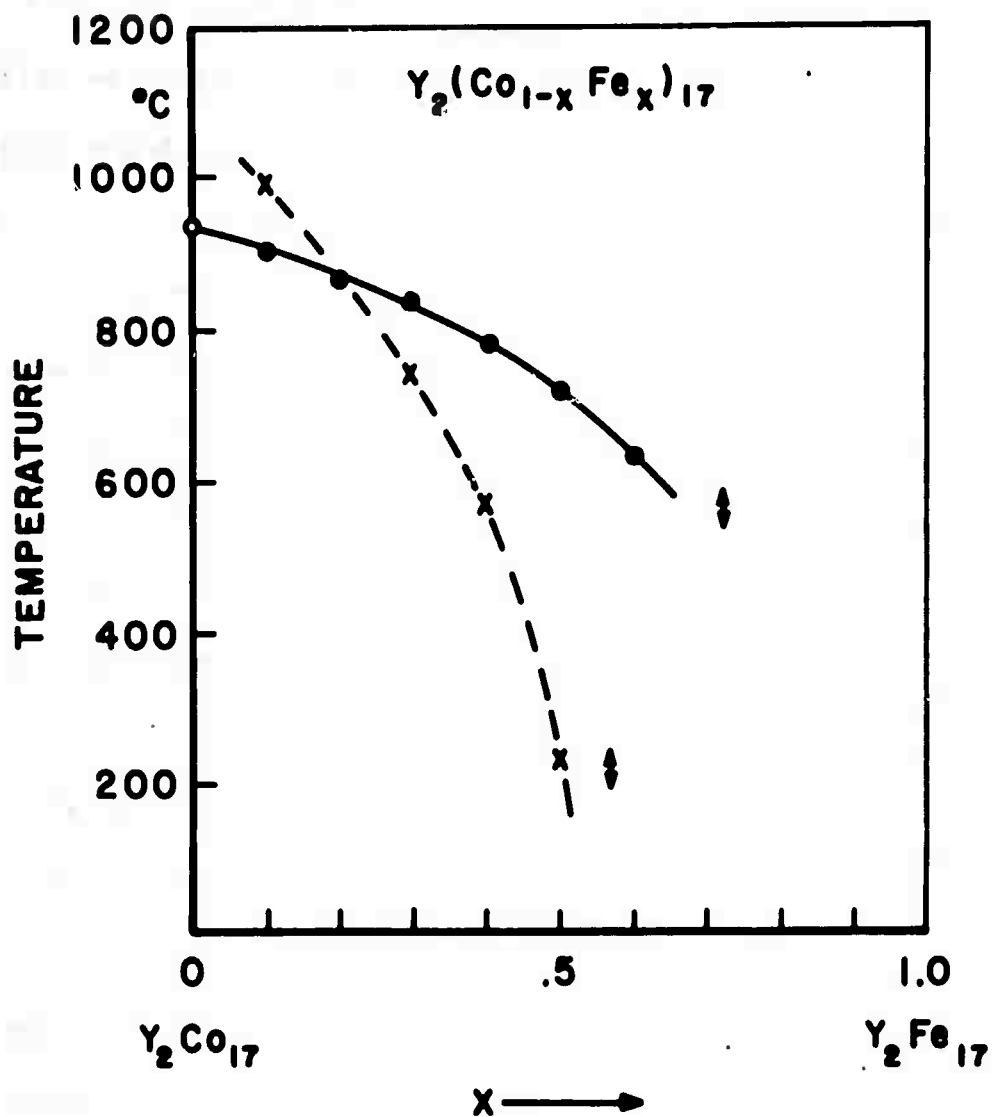
Figure 3. T_c vs. x for $Y_2(Co_{1-x}Fe_x)_{17}$.

(austenite) down to $\sim200^\circ$C or lower in the iron-rich Co-Fe alloys. We shall

pursue these questions further, bringing to bear other tools such as DTA,

x-ray diffraction, and electron microprobe analysis.

The TMA spectra obtained on Sm-Co-Fe alloys on both ends of the

quasi-binary system are relatively uneventful and simple to interpret.

Figure 4 is a summary of the results for this system. Again, the DTA and

the TMA data for T_c agree very closely in the range in which they overlap.

Only the point for x = 0.5 deviates from the smooth line of T_c versus x, but

it is suspected that this is due to a mixup in the alloys and that this sample in

fact had x = 0.4. The analysis will be repeated with a newly-prepared sample.

For some of the samarium alloys in the middle of the system, an additional

rather pronounced step in the TMA curves was observed between 900° and

1000°C, which is 100° to 300° above the Curie point of the $Sm_2(Co, Fe)_{17}$

phases. This event also exhibited a thermal hysteresis, which was generally

small but amounted to 50° difference between heating and cooling for x = 0.3.

This behavior is illustrated in Figure 5, using as an example the alloy

$Sm_2(Co_{.4}Fe_{.6})_{17}$. The physical nature of the transition indicated by this

"TMA event" is not clear at this time, and no corresponding events were

found in differential thermal analysis. It is likely that some of the speculations

made below in connection with the behavior of the cerium alloys apply here,

too.

In the system $Ce_2(Co_{1-x}Fe_x)_{17}$ a much more complex behavior is

observed. For alloys in the middle of the quasi-binary system, several
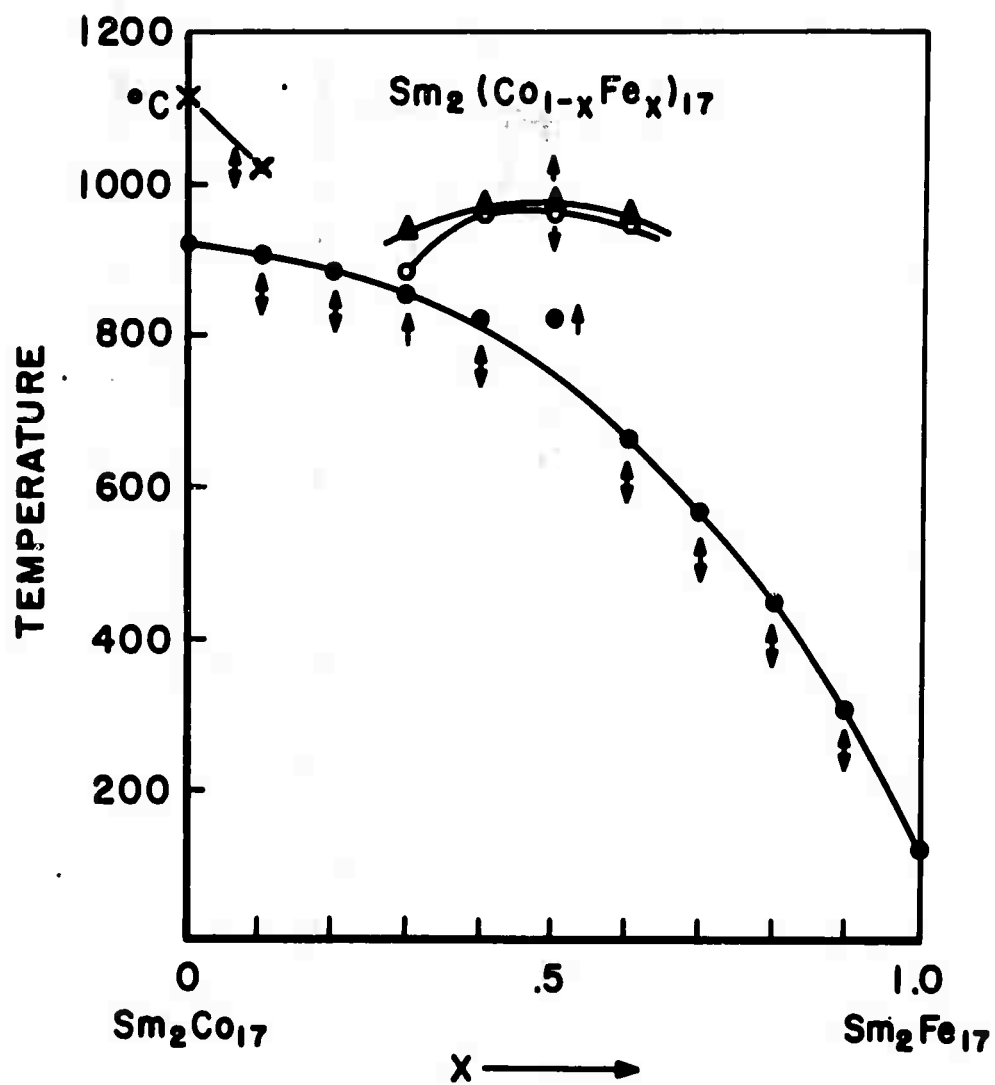
Figure 4. T_c vs. x for $Sm_2(Co_{1-x}Fe_x)_{17}$.

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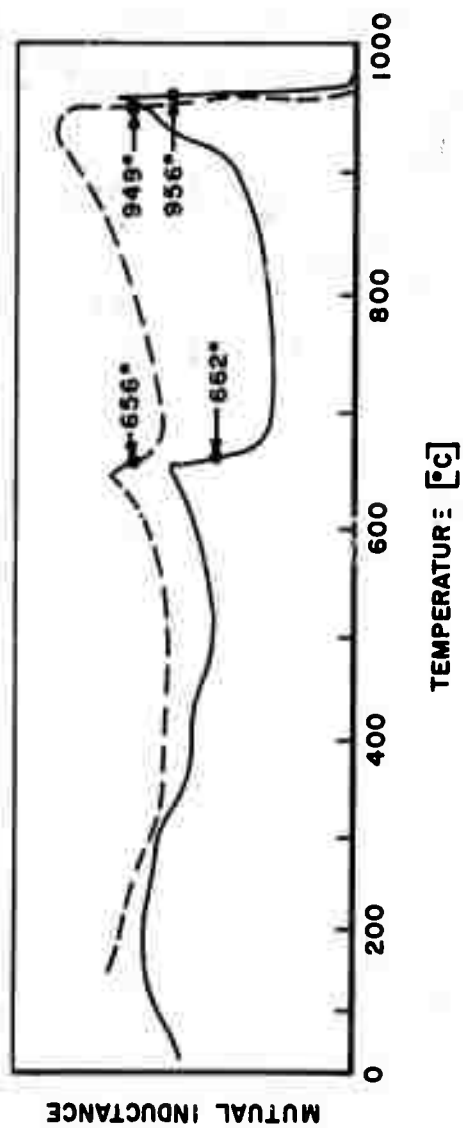
Figure 5. TMA spectrum of $Sm_2(Co_{.4}Fe_{.6})_{17}$ alloy. Solid line is the heating curve; dashed line is the cooling curve.

pronounced steps in the temperature dependence of the initial permeability are seen in the TMA spectra. This is illustrated in Figure 6, a TMA spectrum for $Ce_2(Co_{.4}Fe_{.6})_{17}$. We believe the lowest-temperature step to correspond to the Curie point proper of the rhombohedral 2-17 phase. Note that it is observed only on heating, not on cooling. It is followed by a minor wiggle in the curve, and then another pronounced maximum followed by a sharp step down. This upper transition occurs on heating around 800° to $850^\circ C$ in several of the alloys, but $100-200^\circ$ lower on cooling. Figure 7 summarizes the various TMA events found in the alloys of this system. This complex and irreversible behavior is so far unexplained. Some preliminary x-ray work[11] appears to support the reasoning that the 2-17 compound becomes unstable upon heating somewhere between 750° and $850^\circ C$, that is dissociates into a $Ce(Co,Fe)_2$ phase and an iron-cobalt solid solution alloy, and that this phase transition is irreversible under the conditions of our TMA cycle. However, it is also possible that an oxidation reaction of the powder used in the TMA plays a major role. Clarification of the matter will require additional experimentation using metallography, x-ray diffraction and magnetic measurements. However, this problem has so far been neglected because its solution seems to be of secondary importance for the attainment of the goal of the contract.

Table I is a listing of all the heating and cooling cycles performed on $R_2(Co,Fe)_{17}$ alloys to date. It gives details of the heat treatment of each
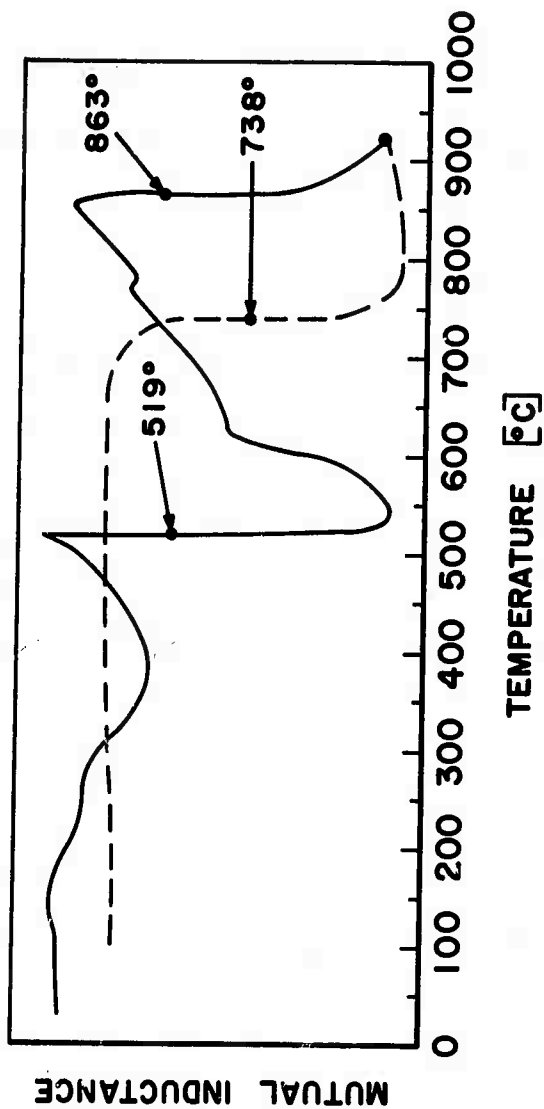
Figure 6. TMA spectrum of $Ce_2(Co_{.4}Fe_{.6})_{17}$ alloy. Solid line is the heating curve; dashed line is the cooling curve.

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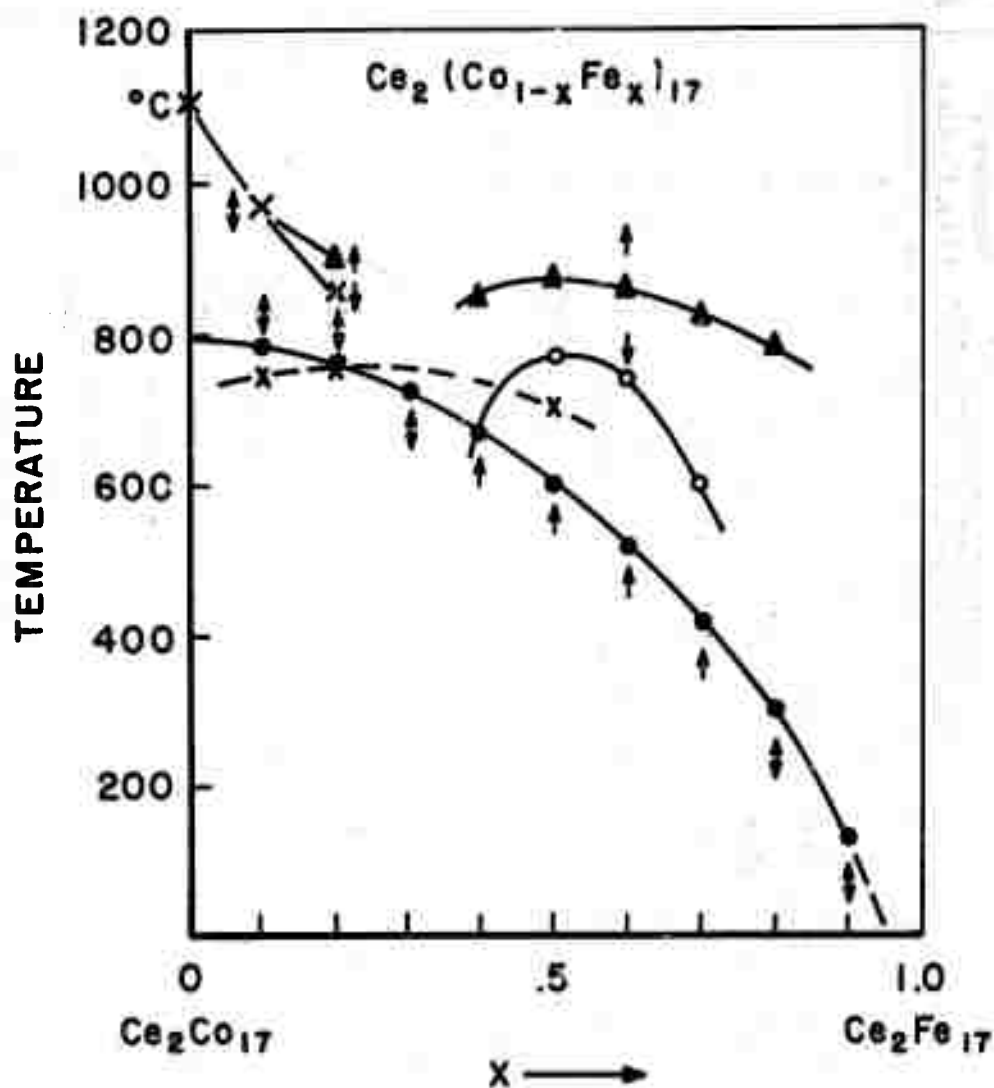
Figure 7. T_c vs. x and temperatures of other irregularities in the TMA spectra of $Ce_2(Co_{1-x}Fe_x)_{17}$ phases.

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TABLE I

LIST OF $R_2(Co,Fe)_{17}$ ALLOYS THERMOMAGNETICALLY ANALYZED

| Alloy Code	Alloy Composition	Heat Treatment Time (hrs)	Heat Treatment Temp. (°C)	Number of TMA Cycles	Peak Temperature Reached in TMA (°C)
AR-757	$Y_2(Co_{.9}Fe_{.1})_{17}$	6	1050	1	1032
AR-766	$Y_2(Co_{.8}Fe_{.2})_{17}$	6	1050	1	1017
AR-773	$Y_2(Co_{.7}Fe_{.3})_{17}$	7	1050	1	1017
AR-777	$Y_2(Co_{.6}Fe_{.4})_{17}$	6	1200	1	1021
AR-787	$Y_2(Co_{.5}Fe_{.5})_{17}$	6	1200	2	1040
AR-899	$Y_2(Co_{.4}Fe_{.6})$	70	1150	1	1055
AR-789	$Sm_2(Co_{.9}Fe_{.1})_{17}$	6	1200	3	1121
AR-815	$Sm_2(Co_{.8}Fe_{.2})_{17}$	18	1200	1	1134
AR-816	$Sm_2(Co_{.7}Fe_{.3})_{17}$	18	1200	1	1139
AR-827	$Sm_2(Co_{.6}Fe_{.4})_{17}$	20	1200	1	1010
AR-828	$Sm_2(Co_{.5}Fe_{.5})_{17}$	20	1200	2	1040
AR-883	$Sm_2(Co_{.4}Fe_{.6})_{17}$	90	1100	2	981
AR-882	$Sm_2(Co_{.3}Fe_{.7})_{17}$	90	1100	1	658
AR-847	$Sm_2(Co_{.2}Fe_{.8})_{17}$	30	1150	1	625
AR-848	$Sm_2(Co_{.1}Fe_{.9})_{17}$	30	1150	1	400
AR-755	$Ce_2(Co_{.9}Fe_{.1})_{17}$	6	1050	3	1023
AR-833	$Ce_2(Co_{.9}Fe_{.1})_{17}$	18	1100	1	1014
AR-764	$Ce_2(Co_{.8}Fe_{.2})_{17}$	6	1050	2	1023

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TABLE I (concluded)

LIST OF $R_2(Co,Fe)_{17}$ ALLOYS THERMOMAGNETICALLY ANALYZED

Alloy Code	Alloy Composition	Heat Treatment		Number of TMA Cycles	Peak Temperature Reached in TMA (°C)
		Time (hrs)	Temp. (°C)		
AR-834	$Ce_2(Co_{.8}Fe_{.2})_{17}$	18	1000	1	998
AR-771	$Ce_2(Co_{.7}Fe_{.3})_{17}$	7	1050	1	866
AR-835	$Ce_2(Co_{.7}Fe_{.3})_{17}$	18	1100	1	1021
AR-775	$Ce_2(Co_{.6}Fe_{.4})_{17}$	6	1050	3	911
AR-785	$Ce_2(Co_{.5}Fe_{.5})_{17}$	7	1050	4	916
AR-840	$Ce_2(Co_{.4}Fe_{.6})_{17}$	18	1000	4	921
AR-841	$Ce_2(Co_{.3}Fe_{.7})_{17}$	18	1000	2	931
AR-842	$Ce_2(Co_{.2}Fe_{.8})_{17}$	18	1000	2	915
AR-843	$Ce_2(Co_{.1}Fe_{.9})_{17}$	18	1000	2	908

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alloy before the start of the thermomagnetic analysis and the highest temperature to which the TMA was carried. It identifies the alloys by the numbers assigned when they were prepared.

D. MAGNETIZATION MEASUREMENTS
    (Mildrum, Walsh, Strnat) .

Magnetization measurements were made with the oscillating specimen magnetometer on loose powder samples of $R_2(Co_{1-x}Fe_x)_{17}$ phases to determine the room-temperature saturation. Many samples in five quasi-binary systems were measured. Tentative results are shown in Table II. The comparison ranges include those for which easy-axis behavior was found.

TABLE II
TENTATIVE RESULTS OF SATURATION MAGNETIZATION MEASUREMENTS ON $R_2(Co_{1-x}Fe_x)_{17}$ PHASES

R	x(Fe Fraction)	σ (emu/g)[*]
Sm	0 - 0.5	109 - 143
Pr	0 - 0.5	128 - 159
Ce	0 - 0.4	103 - 130
Y	0 - 0.5	125 - 150
MM	0.1 - 0.5	118 - 145

[*]Values of σ correspond to the listed extremes of x.

For the quantitative study of crystal anisotropy, magnetically oriented, epoxy-bonded powder samples were made of the same alloys. Easy-axis and hard-axis magnetization curves were measured on these in

fields up to 20 kOe. Figure 8 shows three sets of such magnetization curves measured on three different alloys in the $Sm_2(Co_{1-x}Fe_x)_{17}$ alloy system, namely, the terminal compound Sm_2Co_{17} and the alloys for x = 0.4 and 0.5 which are near the end of the easy-axis region. The curves were measured up to 20 kOe and extrapolated beyond this point. While it was found that smaller iron additions of x = 0.1 and 0.2 increased the anisotropy field slightly above the value of $H_A \approx$ 60-70 kOe of Sm_2Co_{17}, iron additions as high as x = 0.4 and 0.5 bring a reduction of the crystal anisotropy. However, the anisotropy field values are very substantial up to x = 0.5. This indicates that there is a realistic chance that excellent permanent magnets may be produced on the basis of $Sm_2(Co_{1-x}Fe_x)_{17}$ phases.

Figure 9 shows similar sets of easy-axis and hard-axis magnetization curves for three Pr-Co-Fe alloys. Here, the anisotropy field is highest in the range x = 0.3 to 0.5. The highest values of the anisotropy field in this system are only between 20 and 30 kOe, that is, less than half of those found in the samarium system.

Figure 10 shows magnetization curves for aligned powders of three mischmetal-cobalt-iron alloys. Here, the maximum of the anisotropy occurs for x = 0.3, and even this highest anisotropy field is only on the order of 10 kOe, substantially smaller than the anisotropy fields for the praseodymium or samarium systems.

For the $R_2(Co, Fe)_{17}$ phases, as for the RCo_5 phases, it appears that samarium has a certain "magic" quality of being able to induce very high crystal anisotropy. The anisotropy fields measured on these 2-17 phases
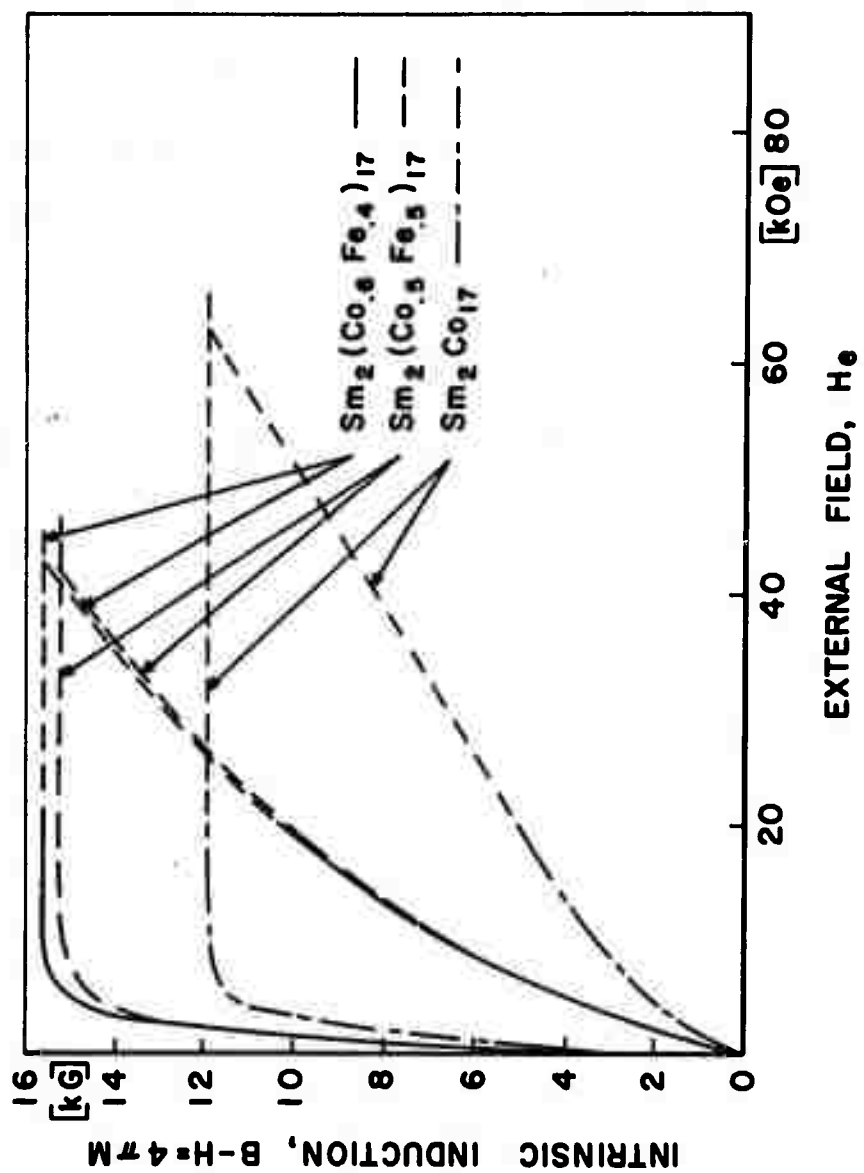
Figure 8. Easy-axis and hard-axis magnetization curves measured on oriented powders of three $Sm_2(Co_{1-x}Fe_x)_{17}$ alloys.

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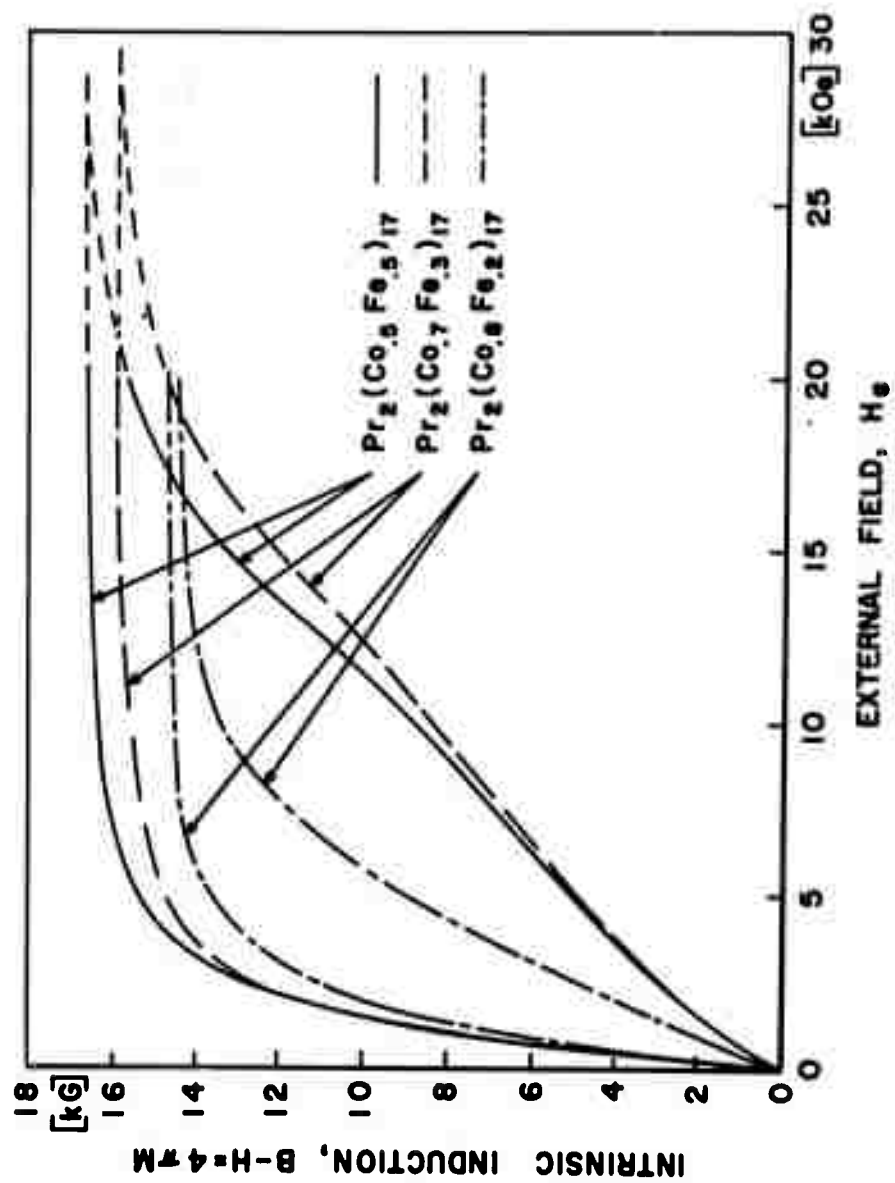
Figure 9. Magnetization curves measured on oriented powders of three $Pr_2(Co_{1-x}Fe_x)_{17}$ alloys.
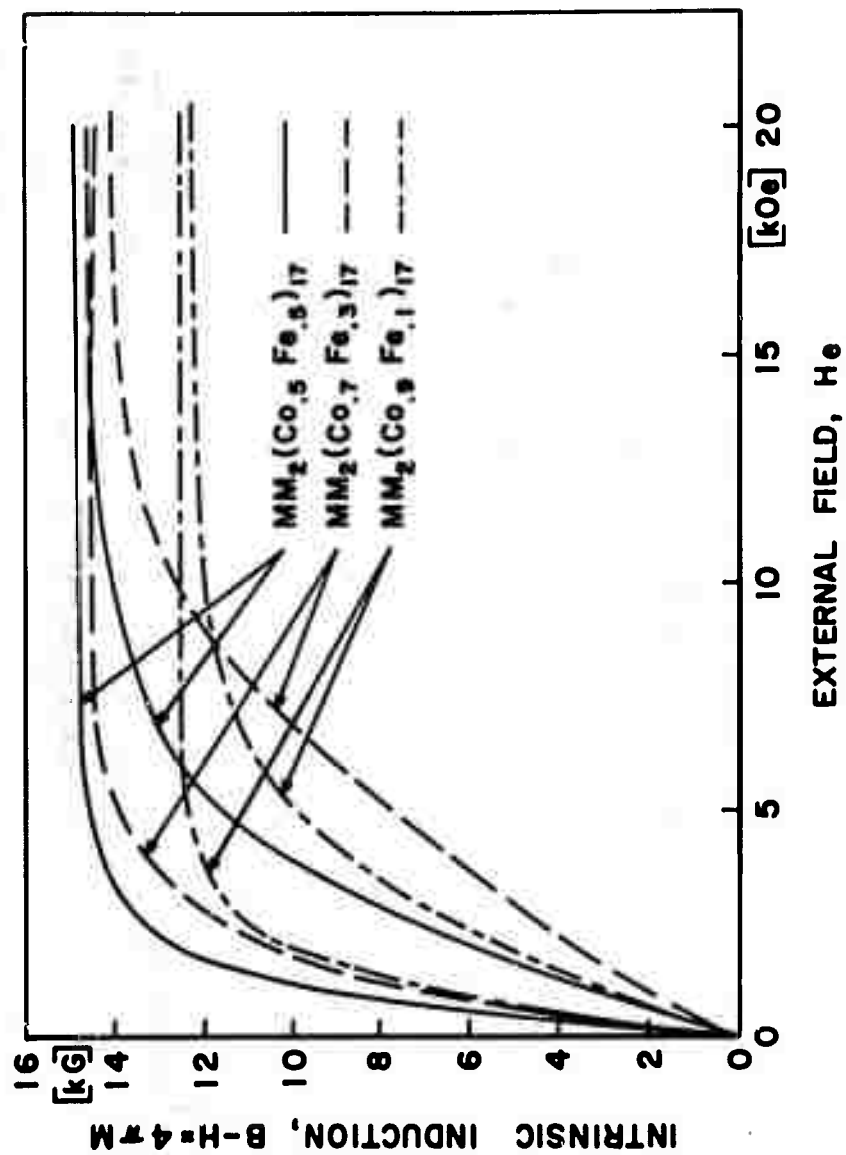
Figure 10. Magnetization curves measured on oriented powders of three $MM_2(Co_{1-x}Fe_x)_{17}$ alloys.

are substantially lower than those of the RCo_5 compounds. However, if we compare them with the value of the anisotropy field of barium ferrite, for which H_A = 17 kOe, they appear nevertheless quite respectably high. Considering that barium ferrite has become a highly successful commercial permanent magnet, we must indeed give the $R_2(Co, Fe)_{17}$ compounds serious consideration, and especially, we must consider the Sm-Co-Fe alloys as very promising candidates for second-generation rare earth permanent magnets.

Early attempts to produce high coercivity in fine powders of Sm_2Co_{17} by grinding did not have encouraging results. The highest $_MH_c$ values achieved were only between 1000 and 2000 Oe. But it seems that by properly applying the present knowledge about the liquid-phase sintering of RCo_5 compound magnets, it should be possible to bring about intrinsic coercive forces which are a substantial fraction of the anisotropy field and thus high enough to exploit the high energy-product potential of the 2-17 phases.

E.   THE PROSPECTS FOR $R_2(Co, Fe)_{17}$ MAGNETS

We have conducted some preliminary experiments trying to sinter ball milled Sm_2Co_{17} powders to which the commonly used 60% Sm/40% Co alloy was added as the sintering aid. In these experiments we have used as the guiding hypothesis the concept that, during sintering, epitaxial shells of a compound richer in the rare earth can form around the core of the base metal alloy, and that effective domain wall pinning can take place in these epitaxial layers.[12] While the concept was first invented to explain some

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observations during the sintering of $PrCo_5$ with a praseodymium-rich sintering aid, it can certainly be applied also to the system in which Sm_2Co_{17} is the base metal. If a samarium-rich sintering aid is used, the first epitaxial shell to form would be $SmCo_5$. Since $SmCo_5$ has the highest anisotropy known, any imperfections in this shell should be very effective pinning sites. We were most encouraged to find intrinsic coercive forces up to $_MH_c$ = 9600 Oe in these initial, and very unsystematic, experiments. We take these results as strong encouragement that, eventually, it should indeed be possible to produce permanent magnets from 2-17 alloys which will have energy products in excess of those of the RCo_5 magnets.

While it is very desirable for many applications to have intrinsic coercive forces ($_MH_c$, in Oe) in excess of the value of the residual magnetization (B_r, in G), energy products near the theoretical limit of $(B_s/2)^2$ can in principle be achieved with coercive forces which are only slightly in excess of $B_s/2$. For the example of Sm_2Co_{17}, which has a saturation of $4\pi B_s$ = 12 kG, a coercivity $_MH_c$ >6 kOe should be sufficient to permit energy products approaching 36 MGOe, provided all other factors can be optimized.

In view of the favorable experimental results reported above, we are encouraged to indulge in some speculations about the energy products one may hope to achieve with magnets based on the 2-17 phases. Let us first consider Figure 11 which shows the room temperature saturation values for all binary R_2Co_{17} and R_2Fe_{17} compounds and, for comparison, those of the RCo_5. We can see that the maximum values which occur for
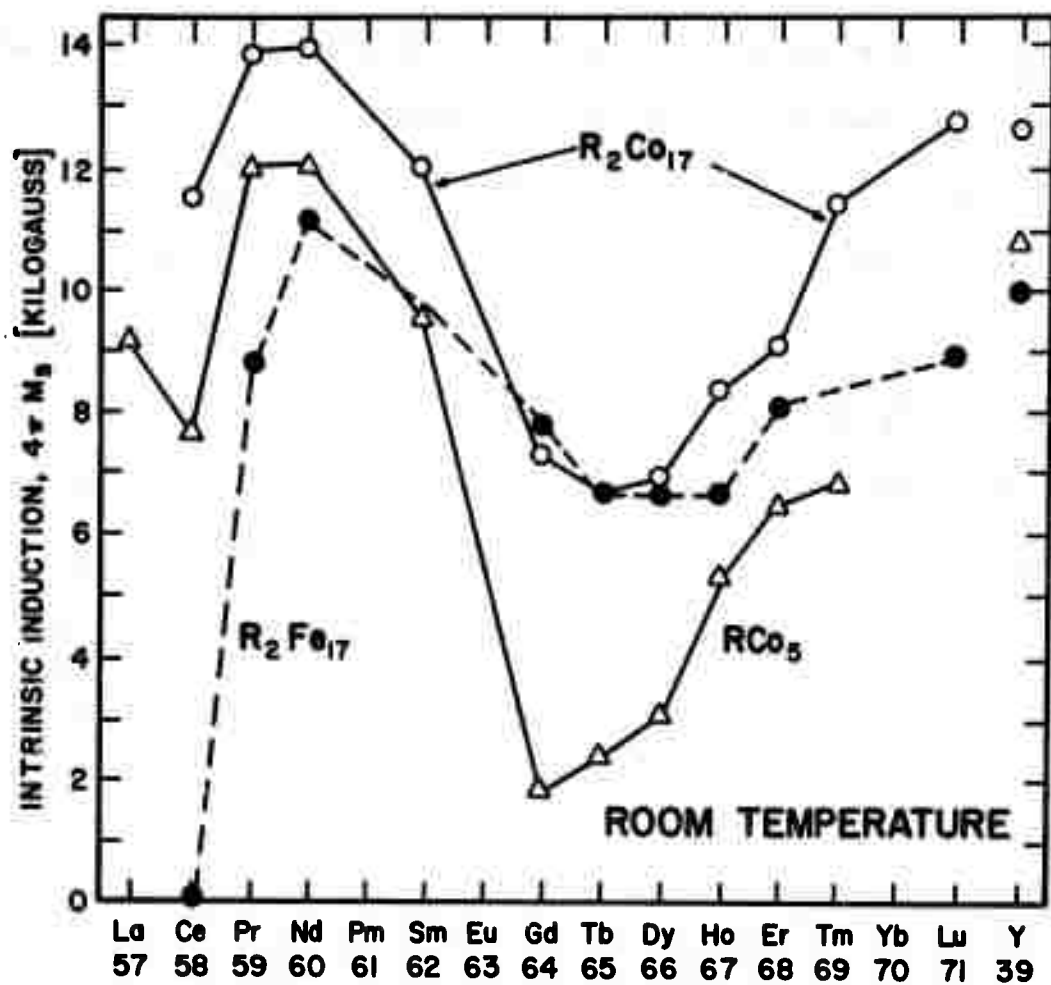
Figure 11. Saturation induction values at room temperature for the compounds R_2Co_{17}, R_2Fe_{17}, and RCo_5.

R = Pr and Nd, are B_s = 14 kG. Even the lowest values of any R_2Co_{17} compounds, those for R = Gd, Tb and Dy, are still near 7 kG. Let us remember that this high saturation is combined with high Curie temperatures near 900°C, a very desirable situation indeed. The saturation values for the R_2Fe_{17} phases would also be attractively high (Fig. 11), but their Curie temperatures are quite low, namely T_c < 180°C.

We have seen that mixed phases of the composition of $R_2(Co_{1-x}Fe_x)_{17}$ exist for all light rare earths and for all values of x. We have also seen that in the systems in which R = Y, Ce, Pr, Sm, and MM, the introduction of some iron in the lattice induces easy-axis anisotropy and thus creates favorable conditions for hard magnetic behavior. Let us also remember that we found earlier during the work under this contract that the introduction of iron in these phases in quantities up to $x \approx 0.5$ does not significantly depress T_c. The Curie points remain above 600°C up to this composition in all the alloy systems of interest.

The theoretical limits for the energy product of these mixed phases are even higher than for the corresponding binary R_2Co_{17} compounds. It is well known that $Co_{1-x}Fe_x$ alloys with $x \approx 0.5$ have the highest room-temperature saturation values of any known substance, higher than those of either iron or cobalt (See Fig. 12). The same behavior carries over into the mixed quasi-binary phases $R_2(Co_{1-x}Fe_x)_{17}$ as is also illustrated in Figure 12 for the example $Y_2(Co_{1-x}Fe_x)_{17}$. The higher saturation values in the middle of the quasi-binary system correspond to higher potential energy products.
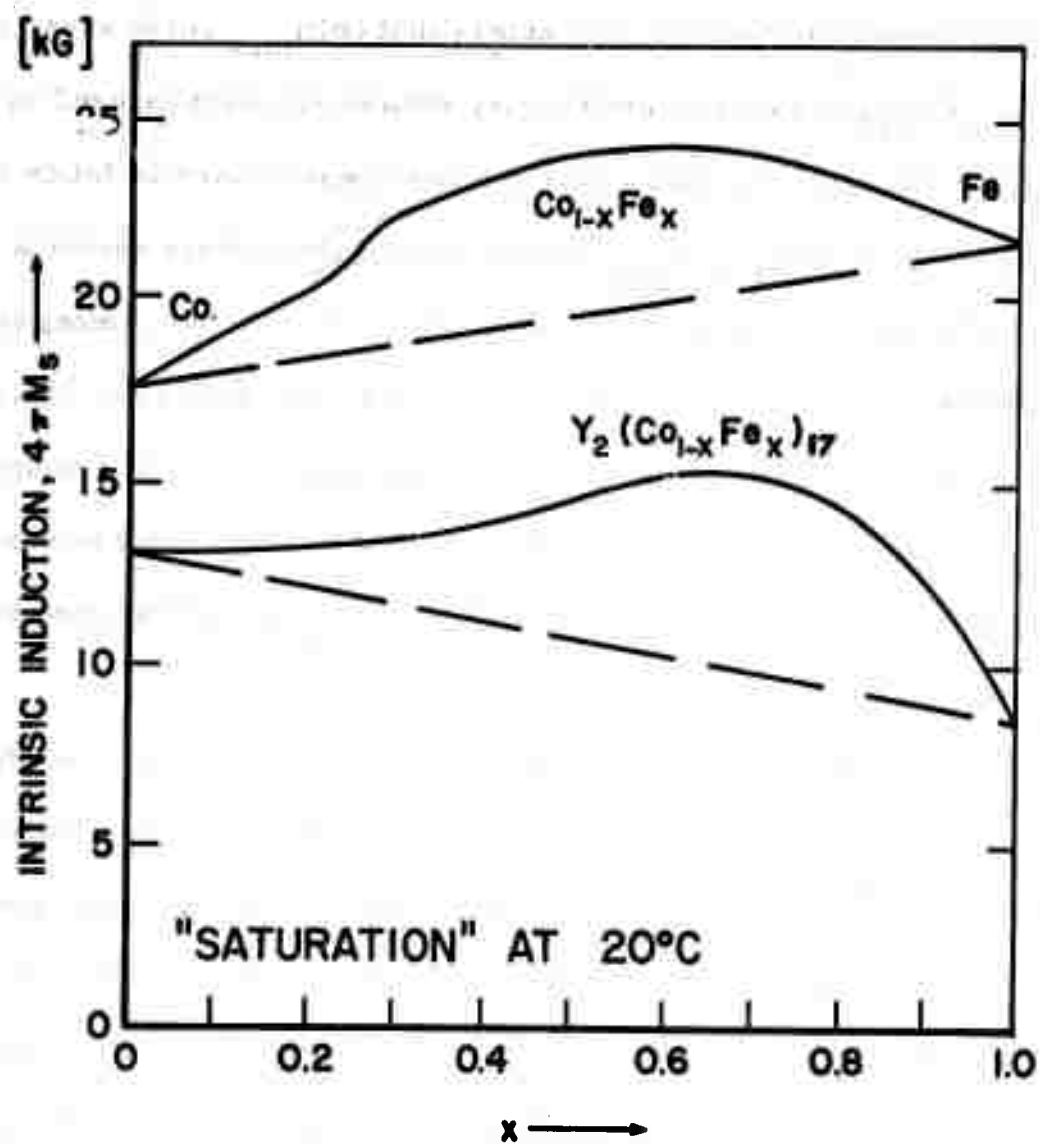
Figure 12. Composition dependence of the room-temperature saturation in the systems Co-Fe and Y_2Co_{17} - Y_2Fe_{17}.

Finally, in Figure 13, we show how the potential static energy products of several of the 2-17 phases compare with the highest energy products available in present commercial magnet types and the best laboratory samples of $SmCo_5$. The upper-limit $(BH)_{max}$ curve shown for $Sm_2(Co_{1-x}Fe_x)_{17}$ is based on preliminary saturation data measured on aligned powder samples. This curve reaches a peak of over 60 MGOe for $x = 0.4$. In the $Pr_2(Co_{1-x}Fe_x)_{17}$ system, even higher values should be possible, but reliable magnetization data are as yet lacking. Among the 2-17 phases even those of the heavier rare earths promise rather high energy products. This is illustrated by the easy-axis type binary cobalt compounds Er_2Co_{17} and Tm_2Co_{17}. Consequently, in contrast to the situation with RCo_5, one could at least tolerate substantial quantities of heavy rare earths in $R_2(Co, Fe)_{17}$ magnet alloys.

It will indeed be a challenging task for the coming years to attempt the practical realization of these hopes and to develop even better rare earth-transition metal magnets than those available at the present time. The next step toward this practical objective must be by systematic sintering studies aimed at creating coercive forces of $_MH_c > B_s/2$ without sacrificing too much of the saturation. The statements made above suggest also that the present investigation of the magnetic properties of ternary R-Co-Fe alloys of the 2-17 type should be expanded to include some phases of the heavy rare earth metals.
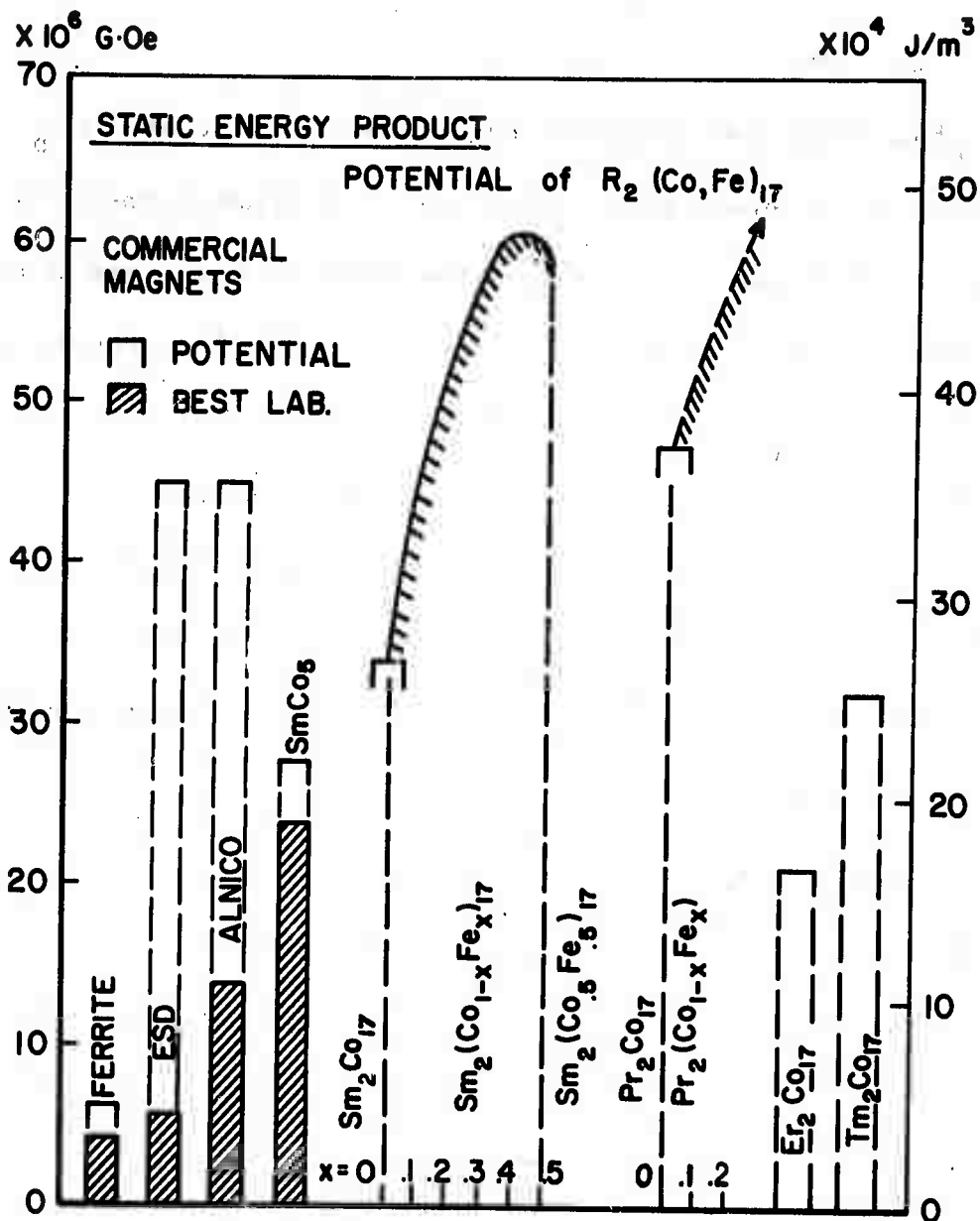
Figure 13. Theoretically possible energy products for magnets made from selected $R_2(Co, Fe)_{17}$ phases compared to best experimental and theoretical values for other magnet types.

SECTION II
METALLURGICAL AND MAGNETIC PROPERTIES
OF SOME $Nd_{1-x}R_xCo_5$ ALLOYS

A.   INTRODUCTION

NdCo$_5$ has the highest saturation magnetization of all of the RCo$_5$ phases, and a high Curie temperature. Moreover, neodymium is one of the most abundant of the rare earth metals. NdCo$_5$ displays an easy c-axis and high magnetocrystalline anisotropy, but only when heated appreciably above room temperature.

We are studying the effect of alloying additions of the type $Nd_{1-x}R_xCo_5$ (when R is any of several of the other rare earth metals) on the transition point of NdCo$_5$ from easy basal plane to easy c-axis anisotropy. We are also studying the effect of these alloying additions on other pertinent magnetic and metallurgical properties.

B.   ALLOY PREPARATION (Leasure, Ray)

The alloys were prepared by arc melting the elemental constituents. Many of these were given subsequent homogenization heat treatments. The same arc melting and homogenization procedures used for R_2Co_{17} alloys were employed. These have been described in a previous report[13]. In each case, the weights of the rare earth elements required to produce nominally stoichiometric $Nd_{1-x}R_xCo_5$ alloys were increased by 2.0 wt.% to compensate for the oxygen present in the elemental constituents. Initial sets of alloys were prepared with R = Ce, Pr, and Y and x-values of 0.25, 0.5 and 0.75 for each set.

C. THERMAL ANALYSIS (Biermann, Ray)

Differential thermal analyses (DTA) were performed on at least one member of each set. The observed melting or peritectic temperatures and Curie points are tabulated in Table III. The melting or peritectic temperatures of the ternary alloys appear to be linear functions of composition, as illustrated in Figure 14. These melting curves were used to determine the maximum annealing temperatures to optimize grain growth conditions for preparing large crystals of the mixed phases.

In contrast to the melting and peritectic temperatures, the Curie temperatures observed by DTA for the $Nd_{1-x}R_xCo_5$ phases do not appear to be monotonic functions of composition. Whether this is actually the case will be checked by the more sensitive TMA measurements.

D. LATTICE CONSTANTS (Geis, Harmer, Ray)

Lattice constants were determined from powder x-ray diffraction patterns obtained with a General Electric XRD-6 diffractometer and Type 700 detector system. The diffraction patterns were obtained with V-filtered Cr K_α radiation. Lattice constant data were refined by the Vogel and Kempter method[14] with the aid of the RCA Spectra 70/40 computer.

Lattice constants for $Nd_{1-x}R_xCo_5$ phases with R = Ce and Pr and x = 0, 0.25, 0.5, 0.75, and 1.0 are given in Table IV. The lattice constants of the mixed $Nd_{1-x}R_xCo_5$ phases do not appear to vary smoothly with composition. This may be because the single phase fields for these alloys are relatively wide and the alloy-to-alloy variations in the total rare earth to

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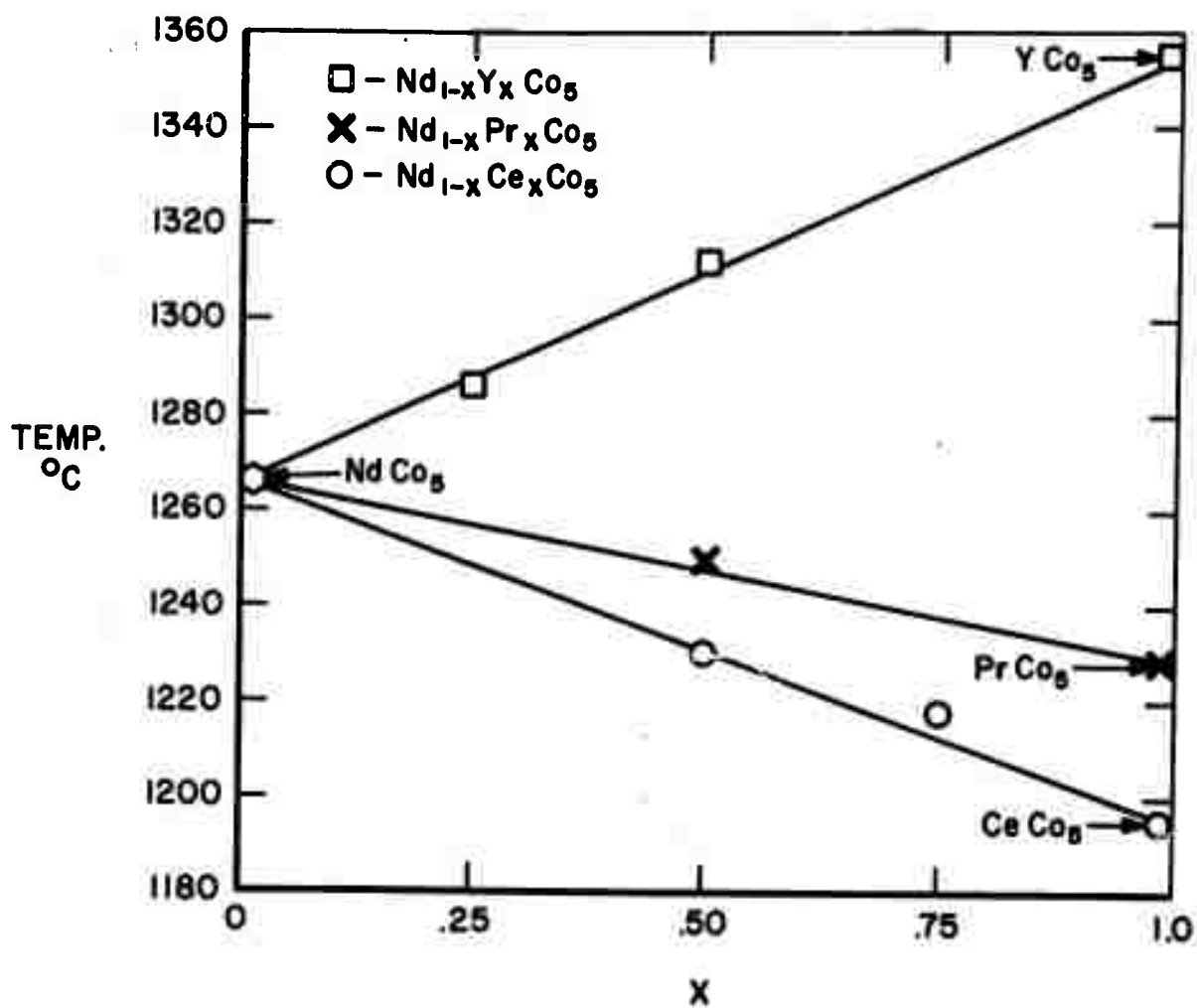
Figure 14.   Melting and peritectic temperatures for $Nd_{1-x}R_xCo_5$ alloys.

TABLE III

THERMAL EVENTS OBSERVED BY DTA FOR

SOME BINARY AND TERNARY RCo_5 ALLOYS

Alloy No.	Nominal Composition	Thermal History	Curie Temperature (°C)	Peritectic or Melting Temp. (°C)
AR-971	YCo_5	168 hrs at 1225°C	657	1353
AR-969	$Nd_{0.5}Y_{0.5}Co_5$	as cast	645	1312
AR-968	$Nd_{0.75}Y_{0.25}Co_5$	as cast	649	1286
AR-874	$PrCo_5$	90 hrs at 1100°C	625	1229
AR-974	$Nd_{0.5}Pr_{0.5}Co_5$	as cast	620 very weak	1250
AR-995	$CeCo_5$	168 hrs at 1100°C	not observed	1195
AR-996	$Nd_{0.25}Ce_{0.75}Co_5$	168 hrs at 1100°C	not observed	1218
AR-978	$Nd_{0.5}Ce_{0.5}Co_5$	as cast	not observed	1230
AR-819	$NdCo_5$	20 hrs at 1050°C	643	1266

TABLE IV

LATTICE CONSTANTS FOR $Nd_{1-x}Ce_xCo_5$ AND $Nd_{1-x}Pr_xCo_5$ PHASES

Alloy No.	Nominal Composition	a_o, Å	c_o, Å	Heat Treatment
AR-967	$NdCo_5$	5.002 ±.001	3.995 ±.001	168 hrs at 1225°C
AR-979	$Nd_{0.75}Ce_{0.25}Co_5$	4.996 ±.001	3.996 ±.001	168 hrs at 1170°C
AR-978	$Nd_{0.5}Ce_{0.5}Co_5$	4.961 ±.001	4.018 ±.001	168 hrs at 1170°C
AR-977	$Nd_{0.25}Ce_{0.75}Co_5$	4.919 ±.001	4.048 ±.001	168 hrs at 1170°C
AR-1000	$CeCo_5$	4.925 ±.001	4.029 ±.001	48 hrs at 1125°C
AR-975	$Nd_{0.75}Pr_{0.25}Co_5$	4.995 ±.001	4.008 ±.001	168 hrs at 1225°C
AR-974	$Nd_{0.5}Pr_{0.5}Co_5$	5.026 ±.001	3.985 ±.001	168 hrs at 1170°C
AR-973	$Nd_{0.25}Pr_{0.75}Co_5$	5.022 ±.001	3.998 ±.001	168 hrs at 1170°C
AR-972	$PrCo_5$	5.017 ±.001	3.999 ±.001	168 hrs at 1170°C

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cobalt ratios (Nd + R/Co) are as significant as the variations in the intra-rare earth ratios (Nd/R). The irregular variation of the Curie temperatures discussed previously may also be due to differences in rare earth to cobalt ratios.

E. PREPARATION OF SINGLE CRYSTALS
(Shanley, Leasure, Kraus, Ray)

Irregularly shaped single crystals of $NdCo_5$, $CeCo_5$, $PrCo_5$, and several mixed $Nd_{1-x}Ce_xCo_5$ and $Nd_{1-x}Pr_xCo_5$ phases measuring from 1..5 to 3.0 mm in diameter have been obtained by long-term annealing of the arc melted alloys. The slightly rare earth-rich alloys were wrapped in tantalum foil and annealed in vacuum for one week (168 hours) at temperatures $50^{\circ}C$ to $100^{\circ}C$ below the peritectic melting temperatures of the RCo_5 phases as determined by DTA. The critical annealing range for rapid grain growth appears to lie between the RCo_5 and R_2Co_7 (or R_5Co_{19}) peritectic decomposition temperatures for the individual alloys. If the alloy is slightly rare earth-rich, then, in this critical temperature range, the small amount of liquid that will be present in the alloy will speed up the diffusion processes markedly. Typical results of the annealing treatment are illustrated in micrographs of a $Nd_{0.5}Ce_{0.5}Co_5$ alloy (AR-978). Figure 15 shows the alloy in the as-cast condition under bright field illumination. This alloy is slightly rare earth-rich. The gray phase is the RCo_5 phase and the lighter phase is either an R_5Co_{19} or an R_2Co_7 phase. The gradation of the gray color of the RCo_5 phase from dark at the centers to light at grain boundaries

suggests "coring" has occurred. The initial portion of the RCo_5 phase to solidify has a slightly different composition than the last. Figure 16 shows the alloy after a homogenization heat treatment of 168 hours at $1170^{\circ}C$. Extensive grain growth has taken place. In this case, the micrograph was taken under polarized light to reveal the magnetic domain patterns in the individual grains or crystals.

The annealed alloys were friable to the extent that the alloys could be broken up either by hand or with a needle used as a pick to fragment off small sections. Single crystals were obtained by selecting the most promising appearing fragments as evidenced by their cleavage fractures. Laue x-ray diffraction patterns were taken to confirm that the selected fragments were indeed single crystals and to orient the crystals for magnetic measurements. Figure 17 is a Laue photograph of a $PrCo_5$ crystal oriented with its c-axis parallel to the x-ray beam. The diffraction spots correspond closely with the size and shape of the crystal.

F.   MAGNETIC CURIE TEMPERATURE MEASUREMENTS
        (Hartings, Mildrum, Strnat)

The composition dependence of the Curie temperature for the systems $Nd_{1-x}Ce_xCo_5$ and $Nd_{1-x}Pr_xCo_5$ was determined using a. c. thermomagnetic analysis (TMA). As usual, we took as the Curie point the temperature of the point of inflection of the steep drop in the curve which follows the Hopkinson maximum on the high-temperature side. Heating and cooling cycles
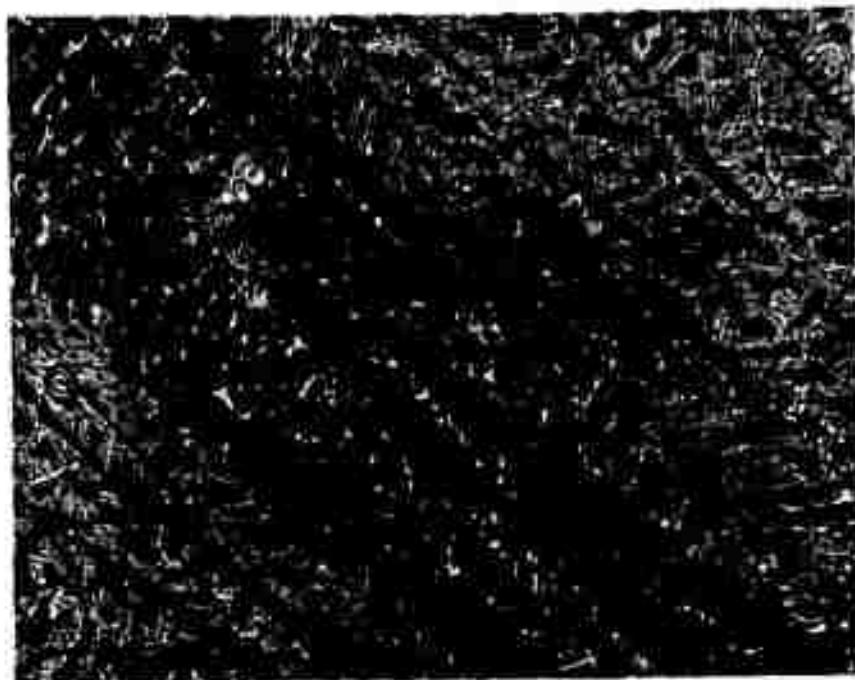
Figure 15. Slightly rare earth rich $Nd_{0.5}Ce_{0.5}Co_5$ alloy (AR-978) as-cast. The gray phase is either an R_5Co_{19} or R_2Co_7 phase. Bright field illumination.
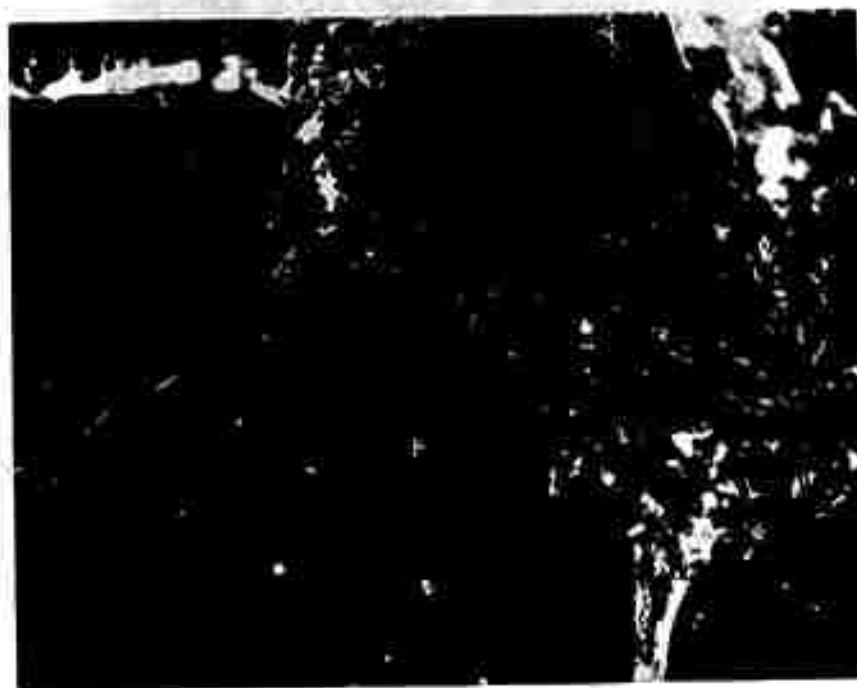
Figure 16. $Nd_{0.5}Ce_{0.5}Co_5$ alloy (AR-978) homogenized for 168 hours at 1170°C. Extensive grain growth is evident. Polarized light was employed to reveal the magnetic domain pattern within the large grains.

Figure 17. Laue photograph of a $PrCo_5$ crystal oriented with its c-axis parallel to the x-ray beam. The diffraction spots correspond closely with the size and shape of the crystal fragment.

were performed in each case at rates of temperature change of ~0.5°C per minute. At this rate, the points of inflection of the heating and cooling curves generally differed by less than 1°C.

Figure 18 shows the results for the quasi-binary system $Nd_{1-x}Ce_xCo_5$. The replacement of neodymium by cerium depresses the Curie temperature slightly faster than one would expect from a linear interpolation between the end points. The results obtained from this series of alloys, which was specifically prepared for this investigation using the same batches of rare earth metals throughout, are nicely consistent. However, significant discrepancies are observed between the T_c values reported here, particularly that for $CeCo_5$, and what we believe to be the best literature values. In the case of $CeCo_5$ we now measure T_c = 460°C, while an investigation done several years ago by L. Salmans at the Air Force Materials Laboratory[15] under the supervision of one of the present authors gave T_c = 374°. Salmans' value was approximately 50° and 90° lower, respectively, than the two Curie point determinations reported in the literature before the data of his measurement.[16,17] In preparing the $CeCo_5$ alloy for Salmans (his material was supplied by the University of Dayton) care had been taken to use the purest cerium metal available. Since the Curie point of $CeCo_5$ is very much lower than that of any other RCo_5 (including the immediate neighbors of $CeCo_5$, namely, $LaCo_5$ and $PrCo_5$) the presence of any rare earth impurity in the cerium used would have the effect of increasing the Curie point. Thus, we may attribute the higher
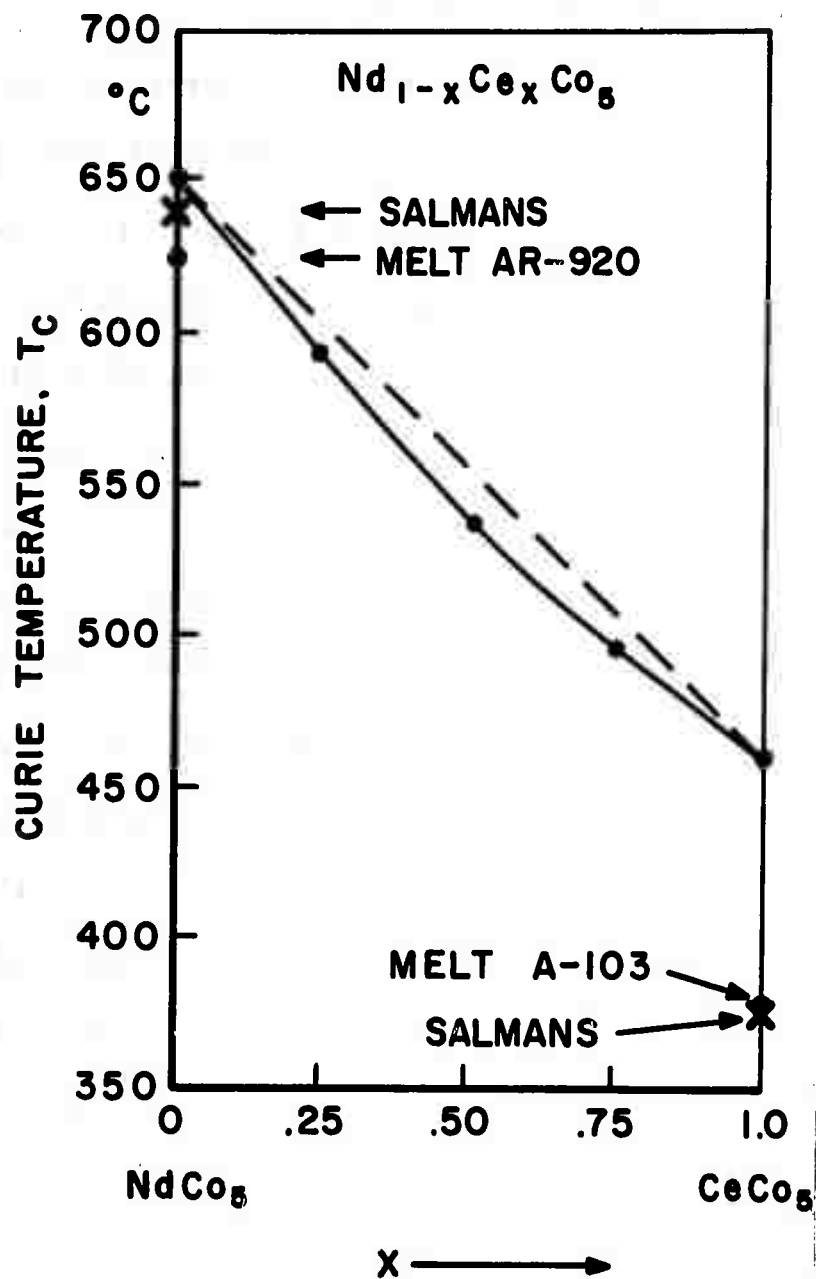
Figure 18. Results of Curie point measurements by TMA in the alloy system $Nd_{1-x}Ce_xCo_5$.

T_c measured now to the presence of relatively large amounts of rare earth impurities, most likely lanthanum, in the cerium metal used in the present investigation.

In interpreting the extraordinarily low value measured by Salmans at the time, we had suggested a different explanation. It is well known that in $CeCo_5$ -- as in other cerium compounds -- the magnetic order is strongly enhanced by relatively moderate applied d.c. fields of only several kOe, and therefore the apparent Curie temperature is shifted upward rather strongly by such fields. Since the earlier literature values for T_c of $CeCo_5$ had been derived from magnetization vs. temperature curves measured in d.c. fields on the order of 10 kOe, we had thought that the proper extrapolation to zero field had been neglected and the Curie temperature therefore overestimated. While this may indeed have been the case, this argument cannot be used to explain the high Curie point of $T_c = 460^{\circ}C$ obtained in our present series of measurements, since we used the same technique as Salmans, applying only very small a.c. fields of the order of 1 Oersted.

To shed some light on this puzzle, TMA was performed on a sample of still another $CeCo_5$ alloy (A-103) which had been obtained from the Th. Goldschmidt Company in Germany as a raw material for the experimental fabrication of permanent magnets. TMA of this alloy yielded a value of $T_c = 378^{\circ}C$, in close agreement with the number reported by Salmans and 80° lower than our other value. Apparently the Goldschmidt alloy was prepared from high purity cerium, while the cerium used in the preparation of our own alloy series was contaminated with other rare earth metals.

Unfortunately, it is typical to find this kind of impurity variation in the commercially traded rare earth metals regardless of the purity claims made by the producer.

A similar, although much less severe, discrepancy was found for the $NdCo_5$. In this case, we measured $T_c = 652^{\circ}C$ while Salmans had reported $640^{\circ}C$. Again, we performed TMA on two other alloys which had previously been prepared at the University of Dayton from neodymium of different origin. The results were $T_c = 625^{\circ}C$ and $T_c = 623^{\circ}C$, about 25° lower than our initial value and somewhat below the value reported by Salmans et al. Here, it is likely that our present neodymium is of higher purity relative to other rare earths than that used by Salmans or in our own older alloys. The rare earth impurities most likely to be found in Nd metal are Pr and Ce, and since the 1-5 compounds of both of these have lower Curie points than $NdCo_5$, their presence would tend to depress T_c.

The results of the Curie point measurements in the system $NdCo_5$-$PrCo_5$ are shown in Figure 19. Here, we find a value of $T_c = 619^{\circ}C$ for pure $PrCo_5$, compared with $616^{\circ}C$ reported by Salmans and $620^{\circ}C$ measured by us on another older $PrCo_5$ alloy which had been prepared from different raw material for a different purpose. These relatively small discrepancies are again attributable to the different impurity content of the rare earth component used. From the rather incomplete data shown in Figure 19 it appears that the substitution of Pr for Nd in $NdCo_5$ causes the Curie point to drop fairly rapidly at first so that the measured T_c values fall substantially

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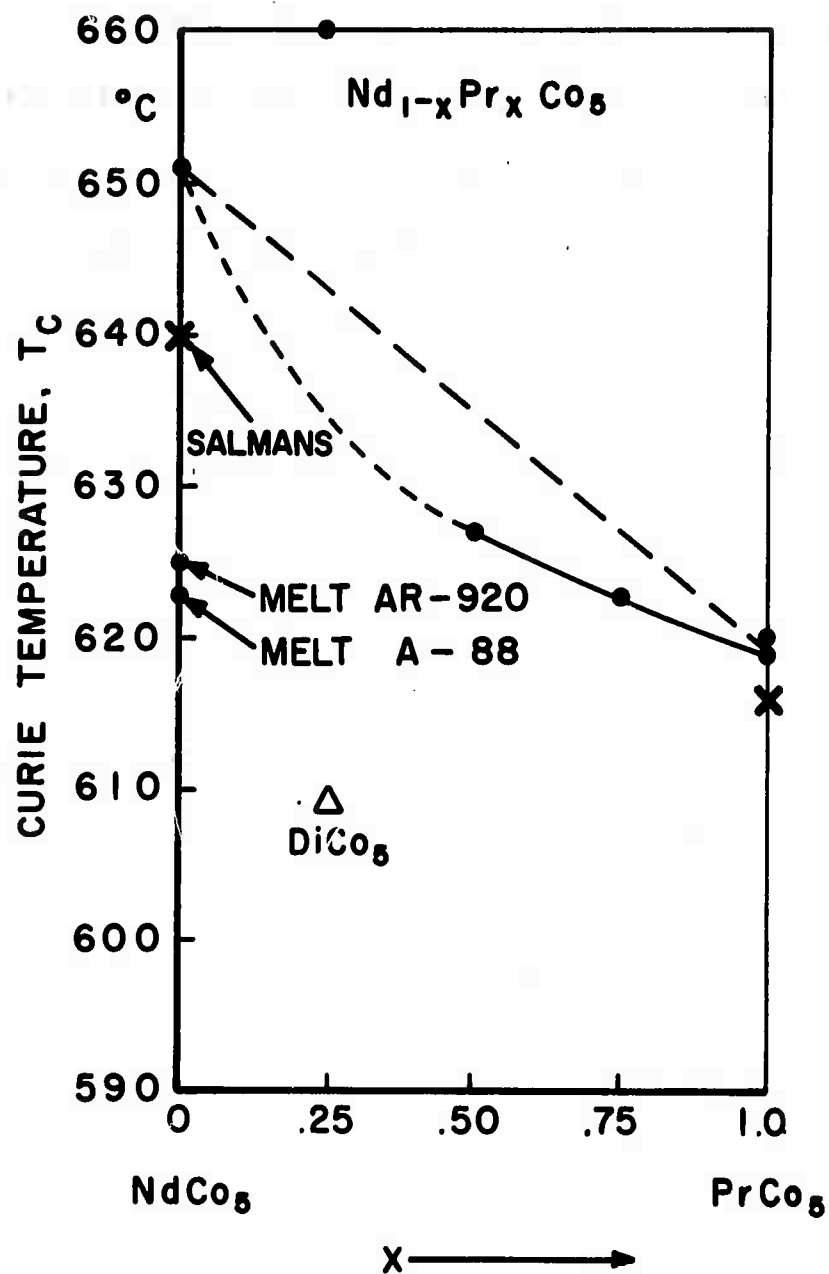
Figure 19. Results of Curie point measurements by TMA
in the alloy system $NdCo_5$ - $PrCo_5$.

below the straight line connecting the end points for $NdCo_5$ and $PrCo_5$. However, it must be noted that the point for x = 0.25 is far out of line for reasons unknown. We have to repeat this measurement and fill in points for other values before firm conclusions can be drawn.

Since the commercial rare earth mixture traded under the name didymium (Di) is normally a mixture of 75% Nd and 25% Pr, we decided to make a thermomagnetic analysis on an alloy $DiCo_5$ prepared with didymium obtained from the Ronson Metals Corporation. The Curie point of this alloy fell about 30° below the expected value; it was $T_c = 609^\circ C$. This could indicate the presence of substantial amounts of cerium as an impurity in this commercial didymium.

Table V lists all the RCo_5 alloys on which thermomagnetic analysis was performed, together with the heat treatment each alloy was given before TMA. Where known, the origin of the rare metal used in alloying is identified, and the identification code assigned each alloy at the University of Dayton is also listed to facilitate future cross reference with other measurements which are now in progress and will be reported later.

TABLE V

LIST OF RCo$_5$ ALLOYS THERMOMAGNETICALLY ANALYZED

Alloy Code	Alloy Composition	Heat Treatment		Number of TMA Cycles	Peak Temperature Reached in TMA (°C)
		Time (hrs)	Temp. (°C)		
AR-967	NdCo$_5$	168	1225	2	726
AR-979	(Nd$_{.75}$Ce$_{.25}$)Co$_5$	168	1170	1	647
AR-978	(Nd$_{.5}$Ce$_{.5}$)Co$_5$	168	1170	1	592
AR-977	(Nd$_{.25}$Ce$_{.75}$)Co$_5$	168	1170	1	614
AR-976	CeCo$_5$	168	1170	3	569
AR-975	(Nd$_{.75}$Pr$_{.25}$)Co$_5$	168	1170	2	715
AR-974	(Nd$_{.5}$Pr$_{.5}$)Co$_5$	168	1170	3	707
AR-973	(Nd$_{.25}$Pr$_{.75}$)Co$_5$	168	1170	1	664
AR-972	PrCo$_5$	168	1170	1	681
A-200	DiCo$_5$			3	669
A-103	CeCo$_5$			3	835
AR-920	NdCo$_5$	24	1100	1	687
A-88	NdCo$_5$			1	679
AR-659	PrCo$_5$			1	681

SECTION III

METALLURGY OF THE R_5Co_{19} PHASES

A.   INTRODUCTION

In Technical Report AFML-TR-71-210,[9] we reported a new phase

in the praseodymium-cobalt alloy system containing between 79 and 80 at.% Co.

Prior to his return to the Centre d'Etudes Nucleaires de Grenoble,

Dr. J. Schweizer determined that the stoichiometry of this phase is Pr_5Co_{19}

and that it exists in two crystallographic modifications: hexagonal with

a_{hex} = 5.053 Å and c_{hex} = 32.47 Å and rhombohedral with a_{rh} = 5.053 Å

and c_{rh} = 48.71 Å.   In 1959, Cromer and Larson[18] suggested that

M_5X_{19} phases might exist and correctly predicted the crystal structure of

these phases. Pr_5Co_{19} has been associated with the higher of two closely

spaced thermal events at $1124^\circ C$ and $1118^\circ C$ in the Pr-Co phase diagram.

Since similar thermal events in the same composition ranges are observed

in the Ce-Co and Nd-Co phase diagram,[19] it seemed likely that the phases

Ce_5Co_{19} and Nd_5Co_{19} also exist.

B.   PREPARATION OF THE ALLOYS (Leasure, Ray)

Three each cerium-cobalt and neodymium-cobalt alloys containing

79.0, 79.5, and 80.0 at.% Co and two praseodymium-cobalt alloys containing

79.2 and 79.5 at.% Co were prepared by arc melting.   The stoichiometric

amounts of Ce and Nd required were increased by 2 wt.% and the Pr by

1 wt.% to correct for oxygen present in the rare earth metals.   All eight

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alloys were wrapped in Ta foil and heated at 1050°C for 24 hours. This heat treatment was sufficient to homogenize the Ce-Co and Pr-Co alloys, but the three Nd-Co alloys required an additional 72 hours at 1100°C to achieve homogeneity.

C.   RESULTS (Biermann, Harmer, Kraus, Shanley, Ray)

The lattice constants, Curie temperatures, peritectic temperatures, and metallographic results are given in Table VI. Lattice constant measurements indicate small solubility ranges extending into the Ce-rich and Pr-rich sides of Ce_5Co_{19} and Pr_5Co_{19}, respectively. Evidence concerning a solubility range for Nd_5Co_{19} is inconclusive. The heat treatments given these alloys resulted in stabilizing the rhombohedral form of the R_5Co_{19} phases. In most of the x-ray diffraction patterns, however, a few faint and diffuse lines were observed which could be assigned to the hexagonal form of R_5Co_{19}. It seems likely that Ce_5Co_{19}, Pr_5Co_{19}, and Nd_5Co_{19} exhibit the hexagonal form only at temperatures very close to the peritectic decomposition temperatures and that the rhombohedral form is stable at lower temperatures. The x-ray powder patterns for the three R_5Co_{19} phases are listed in Table VII.

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TABLE VI

LATTICE CONSTANTS, CURIE TEMPERATURES, AND PERITECTIC TEMPERATURES

FOR Ce_5Co_{19}, Pr_5Co_{19}, AND Nd_5Co_{19}

Alloy No.	Nominal Composition at.%	Lattice Constants		Curie Temperature (°C)	Peritectic Temperature (°C)	Metallography[a]
		a, Å	c, Å			
AR-956	21.0Ce-79.0Co	4.943±1	48.77±3	not observed	1129±5	Ce_5Co_{19} + ~1%Ce_2Co_7
AR-957	20.5Ce-79.5Co	4.938±1	48.69±2	not observed	1130±5	Ce_5Co_{19} + ~1%$CeCo_5$
AR-958	20.0Ce-80.0Co	4.938±1	48.68±2	not observed	1131±5	Ce_5Co_{19} + ~15%$CeCo_5$
AR-936	20.8Pr-79.2Co	5.059±1	48.73±1	422±5	1125±5	Pr_5Co_{19} + ~5%Pr_2Co_7
AR-937	20.5Pr-79.5Co	5.054±1	48.73±1	423±5	1124±5	Pr_5Co_{19} + ~1%$PrCo_5$
AR-953	21.0Nd-79.0Co	5.054±1	48.66±3	443±5	1156±5[b]	Single phase Nd_5Co_{19}
AR-954	20.5Nd-79.5Co	5.054±1	48.68±3	449±5	1155±5[b]	Nd_5Co_{19} + ~5%$NdCo_5$
AR-955	20.0Nd-80.0Co	5.054±2	48.65±2	443±5	1155±5[b]	Nd_5Co_{19} + ~20%$NdCo_5$

a. All alloys homogenized 24 hours at 1050°C. The Nd-Co alloys were homogenized an additional 72 hours at 1100°C.

b. The Nd-Co alloys were made with Nd obtained from Research Chemicals. Similar alloys made with Lunex Nd show the Nd_5Co_{19} peritectic temperature between 1165 and 1170°C.

TABLE VII

POWDER X-RAY DIFFRACTION PATTERNS FOR
Ce_5Co_{19}, Pr_5Co_{19}, AND Nd_5Co_{19}
(V-Filtered $Cr K_\alpha$ Radiation)

hkl	Ce_5Co_{19}		Pr_5Co_{19}		Nd_5Co_{19}	
	Int	d, Å	Int	d, Å	Int	d, Å
0,0,12	VW	4.062	---	-----	W	4.072
0,0,15	VW	3.249	---	-----	--	-----
1,0,13	M	2.816	W	2.846	W	2.847
1,0,14	M	2.701	W	2.726	W	2.729
110	S	2.472	M	2.521	M	2.531
201	S	2.137	M	2.181	M	2.181
1,1,12	S	2.111	S	2.145	S	2.146
0,0,24	S	2.028	M	2.030	M	2.037
1,1,15	M	1.965	W	1.993	W	1.993
2,0,11	M	1.927	---	-----	VW	1.961
1,0,23	W	1.898	VW	1.909	VW	1.910
0,0,27	W	1.8027	W	1.8096	W	1.8050
1,1,24	VW	1.5675	W	1.5828	W	1.5824
2,1,13	W	1.4829	---	-----	W	1.5137
2,1,14	W	1.4688	---	-----	W	1.4947
1,1,27	M	1.4567	W	1.4698	M	1.4675
300	M	1.4266	M	1.4596	M	1.4601
2,0,25	W	1.4400	---	-----	W	1.4536
2,0,26	W	1.4092	VW	1.4236	W	1.4227
3,0,12	VS	1.3452	S	1.3736	M	1.3728
220	S	1.2348	S	1.2635	M	1.2638
1,1,36	---	-----	M^d	1.1933	M^d	1.1913

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